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54 Doped acetylene polymer and process for production thereof.

57 Doped acetylene polymers are produced by immersing an acetylene polymer under an inert gas atmosphere in an organic solvent solution of a dopant selected from the group consisting of a platinum group metal complex, a carbonium salt, an oxonium salt and a parabenzoquinone derivative. According to this process, a doped acetylene polymer having any desired electrical conductivity can be produced and the doped acetylene polymer thus obtained has excellent properties as an organic semiconductor material for solar batteries, various sensors, etc.

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DOPED ACETYLENE POLYMER AND  
PROCESS FOR PRODUCTION THEREOF

1           This invention relates to a process for  
producing a doped acetylene polymer. More particularly,  
this invention relates to a process for the production  
of an acetylene polymer doped with a specific dopant  
5 selected from the group consisting of a platinum group  
metal complex, a carbonium salt, an oxonium salt and  
a parabenzoquinone derivative.

Acetylene polymers are an insulator or semi-  
conductor having an electrical conductivity in the  
10 order of  $10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$  to  $10^{-9} \Omega^{-1} \cdot \text{cm}^{-1}$  [See Macromol.  
Chem. Vol. 175, p. 1565 (1978)]. Heretofore, several  
methods have been proposed to improve the electrical  
conductivity of this polymer. For instance, J. Amer.  
Chem. Soc. Vol. 100, p. 1013 (1978) discloses a process  
15 for increasing the electrical conductivity of an acetylene  
polymer by doping the acetylene polymer in the form of a  
film with HBr,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ , ICl, IBr,  $\text{AsF}_5$ , Na or the  
like as a dopant. The most effective dopants among them  
are  $\text{I}_2$ ,  $\text{AsF}_5$ , etc., and the highest electrical conduc-  
20 tivity obtained by this method is in the order of  $10^2$   
 $\Omega^{-1} \cdot \text{cm}^{-1}$ . A process for doping with a silver salt such  
as  $\text{AgBF}_4$  or  $\text{AgClO}_4$ , or  $\text{FSO}_2\text{OOSO}_2\text{F}$  has been proposed,  
respectively, on page 489 or 1066 of J. Chem. Soc. Chem.  
Comm. (1978). In the former case an electrical  
25 conductivity in the order of  $10^0 \Omega^{-1} \cdot \text{cm}^{-1}$  can be attained,

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1 and in the latter case, an electrical conductivity in  
the order of  $10^2 \Omega^{-1} \cdot \text{cm}^{-1}$  can be obtained. The doping  
with these chemicals is carried out by allowing the  
chemicals in the gaseous state or in the form of a  
5 solution in a solvent to permeate the acetylene polymer,  
because the acetylene polymer is insoluble in the  
chemicals.

The present inventors have made an intensive  
survey of a process for doping an acetylene polymer and  
10 have consequently found that the acetylene polymer can  
be doped with a platinum group metal complex, a  
carbonium salt, an oxonium salt or a parabenzoquinone  
derivative.

An object of this invention is to provide a  
15 novel doped acetylene polymer.

Another object of this invention is to provide  
a novel process for producing the novel doped acetylene  
polymer.

Other objects and advantages of this invention  
20 will become apparent from the following description.

According to this invention, there is provided  
an acetylene polymer doped with a platinum group metal  
complex, a carbonium salt, an oxonium salt, or a  
parabenzoquinone derivative.

25 The doped acetylene polymer of this invention  
can be prepared by immersing an acetylene polymer under  
an inert gas atmosphere in an organic solvent solution  
of the platinum group metal complex, carbonium salt,

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1 oxonium salt or parabenzoquinone derivative.

The process of this invention has the following characteristic advantages, and in view of these advantages, this invention is wide in application field

5 and very valuable from the commercial point of view:

1. The dopant used in this invention is free from corrosiveness and volatility. This is very advantageous for the doping operation, and in addition, the doped acetylene polymer obtained is stable in performance.

10 2. According to the process of this invention, the electrical conductivity of the objective doped acetylene polymer can be regulated to any desired order of value.

3. The doped acetylene compound obtained by the  
15 process of this invention has excellent performance as an organic semiconductor for solar batteries and various sensors.

4. In particular, the acetylene polymer doped with the platinum group metal complex, the carbonium salt or  
20 the oxonium salt is excellent in heat-resistance and light-stability under an inert atmosphere or under vacuum.

The platinum group metal complex used in this invention is a platinum group metal complex active for  
25 substitution reaction with olefines, and includes, for example,  $(\text{PhCN})_2\text{PdCl}_2$ ,  $(\text{COD})\text{PdCl}_2$ ,  $[(\text{C}_2\text{H}_4)\text{PdCl}_2]_2$ ,  $(\text{Ph}_4\text{C}_4)\text{PdCl}_2$ ,  $(\text{COD})\text{PtCl}_2$ ,  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]\text{H}_2\text{O}$ ,  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$ ,  $(\text{PhCN})_2\text{PtCl}_2$ ,  $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ , and

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1 Ru(COD)Cl<sub>2</sub> wherein COD stands for 1,5-cyclooctadiene and  
 Ph<sub>4</sub>C<sub>4</sub> for tetraphenylcyclobutadiene. Palladium complexes  
 such as (PhCN)<sub>2</sub>PdCl<sub>2</sub> and [(C<sub>2</sub>H<sub>4</sub>)PdCl<sub>2</sub>]<sub>2</sub> are preferred as  
 the platinum group metal complex used in this invention.

5 Examples of the carbonium salt and oxonium  
 salt used in this invention include onium salts consist-  
 ing of combinations of the following cations and anions:

Cations: triphenylmethyl ion [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C<sup>+</sup>],  
 tropylium ion (C<sub>7</sub>H<sub>7</sub><sup>+</sup>),  
 10 acyl ion (RCO<sup>+</sup>),  
 dialkoxycarbonium ion [RC(OR')(OR'')<sup>+</sup>],  
 triethyloxonium ion [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>O<sup>+</sup>],

In the above formulas, R, R' and R'' represent  
 independently an organic group, and usually  
 15 alkyls, aryls or aralkyls, and R, R' and R''  
 may be the same or different.

Anions: BF<sub>4</sub><sup>-</sup>, AlCl<sub>4</sub><sup>-</sup>, FeCl<sub>4</sub><sup>-</sup>, SnCl<sub>5</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, PCl<sub>6</sub><sup>-</sup>,  
 SbCl<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>.

Preferable cations are triphenylmethyl ion and  
 20 triethyloxonium ion, and preferable anions are  
 BF<sub>4</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>.

Parabenzquinone derivatives used in this  
 invention include, for example, 2,3-dicyano-5-chloro-  
 parabenzquinone, 2,3-dichloro-5,6-dicyanoparabenz-  
 25 quinone, 2,3-dicyano-5-phenylsulphonylparabenzquinone,  
 2,3-dicyano-5-chloro-6-phenylsulfonylparabenzquinone,  
 and 2,3,5,6-tetracyanoparabenzquinone. Preferable  
 parabenzquinone derivatives are those having the first

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- 1 half wave reduction potential ( $-E_{1/2}$ ) of less than  
-0.2 V at 25°C as measured by saturated calomel  
electrode using  $\text{LiClO}_4$  as a supporting electrolyte in  
acetonitrile. The most preferred parabenzoquinone  
5 derivative is 2,3-dichloro-5,6-dicyanoparabenzoquinone.

Note: The first half wave reduction potential of  
parabenzoquinone derivatives is described in,  
for example, The Chemistry of the Quinoid  
Compounds, Part 2, John Wiley and Sons (1974),  
10 p. 770.

As the organic solvents used in this invention,  
any kind of organic solvent may be used, as far as the  
solvent can dissolve the above-mentioned platinum group  
metal complex, carbonium salt, oxonium salt or

- 15 parabenzoquinone derivative.

As the solvent, there may be mentioned, for  
example, aromatic hydrocarbons such as benzene,  
toluene, xylene and the like; nitro compounds such as  
nitromethane, nitroethane, nitrobenzene and the like;  
20 nitrile compounds such as acetonitrile, benzonitrile,  
and the like; ether compounds such as diethyl ether,  
tetrahydrofuran, dioxane, anisole, and the like; lower  
alcohols such as methanol, ethanol, propanol and the  
like; halogeno compounds such as dichloromethane,  
25 chloroform, chlorobenzene, methylene chloride,  
trifluoroacetic acid, and the like; ester compounds  
such as methyl acetate, ethyl acetate and the like;  
ketone compounds such as acetophenone, acetone and

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1 the like; sulfoxide compounds such as dimethylsulfoxide  
and the like; amide compounds such as N,N-dimethyl-  
formamide and the like; and lower organic acids such  
as acetic acid and the like; and anhydrides of lower  
5 organic acids.

The form of the starting acetylene polymer  
used is not critical, though it may be any of the  
powder, film and fiber. The doping treatment is pre-  
ferably conducted under an inert gas atmosphere, since  
10 the acetylene polymer is unstable against oxygen. For  
instance, the doping is carried out by immersing the  
acetylene polymer in an organic solvent solution of a  
platinum group metal complex, a carbonium salt, an  
oxonium salt or a parabenzoquinone derivative. The  
15 concentration of the solution used for doping is decided  
depending upon the solubility of the dopant used because  
the solubility of the dopant is varied depending on the  
kind of the dopant used. However, there is seen the  
tendency that the higher the concentration used, the  
20 larger the weight increase of the polymer doped in a  
short period of time becomes. The period of immersing  
acetylene polymer may be varied depending upon the  
concentration of the solution used and the temperature  
for the doping treatment. The immersion temperature  
25 is not critical and the immersion treatment may be

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1 effected at any temperature at which the dopant does  
not decompose and the solvent does not solidify.

Generally, the immersion is effected at 10° to 70°C.

The doped acetylene polymer thus prepared  
5 is subjected to measurement of electrical conductivity  
by a 4-probe method. The electrical conductivity of  
the doped polymer varies depending on the kind of  
dopant and the weight increase of the doped acetylene  
polymer. The larger the weight increase of the doped  
10 acetylene polymer, the greater the electrical conduc-  
tivity of the doped acetylene polymer becomes. There-  
fore, the electrical conductivity of the doped  
acetylene polymer can be adjusted by controlling  
the weight increase of the doped acetylene polymer.

15 Furthermore, the doped acetylene polymer is  
also handled preferably under an inert gas atmosphere,  
since the obtained polymer is also unstable against  
oxygen.

This invention is illustrated below referring  
20 to Examples, which are not by way of limitation but by  
way of illustration. The acetylene polymer used in  
the Examples was prepared by the following method:

#### Preparation of acetylene polymer

In a 500-ml glass vessel was placed 1.7 ml of



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1 titanium tetrabutoxide under a nitrogen atmosphere and was  
dissolved in 30 ml of toluene in the vessel. Thereto was  
added 2.7 ml of triethylaluminium with stirring to effect  
reaction. The vessel containing the reaction product  
5 was mounted on a polymerization apparatus, and the  
catalyst solution contained in the vessel was solidified  
by liquid nitrogen in the vessel, after which the  
nitrogen in the vessel was removed by a vacuum pump.  
The temperature of the vessel was returned to room  
10 temperature to vaporize the nitrogen dissolved in the  
solution and then the solution was again solidified by  
liquid nitrogen and evacuated. Thereafter, the vessel  
was kept at a temperature of a dry ice-methanol mixture  
and purified acetylene was introduced into the vessel  
15 under reduced pressure from a gas holder in which the  
acetylene was stored in the static state.

Polymerization occurred at once on the surface  
of the solution and an acetylene polymer in the form of  
a film was formed. Thirty minutes after the introduction  
20 of acetylene, the vessel was taken out of the polymeri-  
zation apparatus and nitrogen gas was introduced into  
the vessel. The catalyst solution was removed from  
the vessel by means of a syringe, and thereafter the  
polymer obtained was dried and washed thoroughly with de-  
25 oxygenated toluene. The toluene was thereafter removed  
by means of a syringe, and the contents of the vessel  
were dried under vacuum to obtain an acetylene polymer  
film.

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1           The electrical conductivity of this acetylene  
polymer film as measured by a 4-probe method was  $10^{-8}$   
 $\Omega^{-1} \cdot \text{cm}^{-1}$ .

#### Example 1

5           An acetylene polymer film was immersed in a  
solution of 0.2 g of  $[(\text{C}_2\text{H}_4)\text{PdCl}_2]_2$  in 20 ml of dried  
deoxygenated chloroform, and allowed to stand at room  
temperature for 24 hrs. This acetylene polymer film  
was thereafter transferred to another vessel, washed  
10 with chloroform and vacuum-dried. The electrical  
conductivity of the doped acetylene film thus obtained  
was  $3 \times 10^{-2} \Omega^{-1} \cdot \text{cm}^{-1}$  as measured by a 4-probe method.  
The doped acetylene polymer in the form of a film was  
subjected to the ESCA (electron spectroscopy for  
15 chemical analysis) measurement to detect only divalent  
Pd. From this fact, it was understood that the  
electrical conductivity of the doped acetylene polymer  
was increased as a result of the acetylene polymer  
having been doped with the Pd compound and the Pd metal  
20 deposited upon decomposition of the complex did not  
participate in the increase in electrical conductivity.

When the doped acetylene polymer was allowed to  
stand for 6 months at  $100^\circ\text{C}$  at a reduced pressure of  $10^{-1}$   
Torr or under natural weather conditions in a glass  
25 container at a reduced pressure of  $10^{-1}$  Torr, substantially  
no change in electrical conductivity was observed.

It is to be noted that, in this Example, all  
the procedures were carried out under a nitrogen

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1 atmosphere so as not to expose the acetylene polymer to air, and the same applies to the subsequent Examples unless otherwise specified.

## Example 2

5 An acetylene polymer film was immersed in a solution of 0.1 g of  $(\text{PhCN})_2\text{PdCl}_2$  in 20 ml of dried deoxygenated methylene chloride and allowed to stand at room temperature for 24 hrs. This acetylene polymer film was then transferred to another vessel, washed with  
10 fresh methylene chloride and vacuum-dried. The doped acetylene polymer film thus obtained had an electrical conductivity of  $3 \times 10^{-3} \Omega^{-1} \cdot \text{cm}^{-1}$ .

## Example 3

An acetylene polymer film was immersed in a  
15 solution of 0.1 g of  $(\text{PhCN})_2\text{PtCl}_2$  in 20 ml of dried deoxygenated methylene chloride and allowed to stand at room temperature for 24 hrs. This acetylene polymer film was then transferred to another vessel and washed with fresh methylene chloride and vacuum-dried. The  
20 electrical conductivity of the doped acetylene polymer film thus obtained was  $7 \times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$ .

## Example 4

An acetylene polymer film was immersed in a solution of 0.1 g of  $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$  in dried deoxygenated  
25 methylene chloride and allowed to stand at room

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1 temperature for 24 hours. This acetylene polymer film  
was thereafter transferred to another vessel, washed  
with fresh methylene chloride and vacuum-dried.

The electrical conductivity of the doped  
5 acetylene polymer film thus obtained was  $5 \times 10^{-5}$   
 $\Omega^{-1} \cdot \text{cm}^{-1}$ .

#### Example 5

An acetylene polymer film was immersed in a  
solution of 0.1 g of  $\text{Ru}(\text{COD})\text{Cl}_2$  in 20 ml of dried  
10 deoxygenated chloroform and allowed to stand at room  
temperature for 24 hrs. This acetylene polymer film  
was thereafter transferred to another vessel, washed  
with fresh chloroform and vacuum-dried.

The doped acetylene polymer film thus  
15 obtained had an electrical conductivity of  $6 \times 10^{-5}$   
 $\Omega^{-1} \cdot \text{cm}^{-1}$ .

#### Example 6

An acetylene polymer film was immersed in a  
dried methylene chloride solution of  $(\text{C}_2\text{H}_5)_3\text{O}^+\text{BF}_4^-$   
20 (0.3 g/10 ml), subjected to deaeration, and then allowed  
to stand at room temperature for 24 hrs. This acetylene  
polymer film was thereafter transferred to another  
vessel, washed with fresh methylene chloride, and  
vacuum-dried. All the procedures were carried out  
25 under an argon atmosphere.

The doped acetylene polymer film thus obtained  
had an electrical conductivity of  $5 \times 10^{-2} \Omega^{-1} \cdot \text{cm}^{-1}$ .

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- 1 When the doped acetylene polymer was allowed to stand for  
6 months at 100°C at a reduced pressure of  $10^{-1}$  Torr or  
under natural weather conditions in a glass container at  
a reduced pressure of  $10^{-1}$  Torr, substantially no change  
5 in electrical conductivity was observed.

## Example 7

- An acetylene polymer film was immersed in a  
dried methylene chloride solution of  $(C_6H_5)_3C^+BF_4^-$   
(0.3 g/10 ml), subjected to deaeration, and allowed to  
10 stand at room temperature for 24 hrs. This acetylene  
polymer film was thereafter transferred to another vessel,  
washed with fresh methylene chloride and dried under  
vacuum. The doped acetylene polymer film thus obtained  
had an electrical conductivity of  $3 \times 10^{-1} \Omega^{-1} \cdot cm^{-1}$ .  
15 All the procedures were carried out under an argon  
atmosphere.

## Example 8

- In 20 ml of dried deoxygenated benzene was  
dissolved 0.1 g of 2,3-dichloro-5,6-dicyanoparabenz-  
20 quinone ( $-E_1/2 = -0.5$  V). An acetylene polymer film was  
immersed in the solution, and allowed to stand at room  
temperature for 24 hrs. This acetylene polymer film was  
thereafter transferred to another vessel and vacuum-dried.  
The doped acetylene polymer film thus obtained had an  
25 electrical conductivity of  $2 \times 10^{-1} \Omega^{-1} \cdot cm^{-1}$ .

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## 1 Example 9

In 20 ml of dried deoxygenated benzene was dissolved 0.1 g of 2,3-dicyano-5-chloroparabenzquinone ( $-E_{1/2} = -0.41$  V). An acetylene polymer film was

5 immersed in the solution and allowed to stand at room temperature for 24 hrs. This acetylene polymer film was transferred to another vessel and vacuum-dried. The doped acetylene polymer film thus obtained had an electrical conductivity of  $5 \times 10^{-3} \Omega^{-1} \cdot \text{cm}^{-1}$ .

## 10 Example 10

An acetylene polymer film was immersed in a solution of 0.1 g of  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$  in 20 ml of dried deoxygenated acetone and allowed to stand at room temperature for 24 hrs. This acetylene polymer film was

15 thereafter transferred to another vessel, washed with fresh acetone and then dried under vacuum. The doped acetylene polymer film thus obtained had an electrical conductivity of  $8 \times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$ .

## Example 11

20 An acetylene polymer film was immersed in a solution of 0.1 g of  $(\text{COD})\text{PdCl}_2$  in 20 ml of dried deoxygenated methylene chloride, and allowed to stand at room temperature for 24 hrs. This acetylene polymer film was thereafter transferred to another vessel, washed

25 with fresh methylene chloride, and then dried under vacuum. The doped acetylene polymer film thus obtained

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1 had an electrical conductivity of  $7 \times 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$ .

Example 12

An acetylene polymer film was immersed in a solution of 0.1 g of  $(\text{COD})\text{PtCl}_2$  in 20 ml of dried deoxyge-  
5 nated fresh methylene chloride, and allowed to stand at room temperature for 24 hrs, after which the acetylene polymer film was taken out of the solution, washed with methylene chloride, and then dried under vacuum. The doped acetylene polymer film thus obtained had an  
10 electrical conductivity of  $2 \times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$ .

Example 13

An acetylene polymer film was immersed in a solution of 0.1 g of  $(\text{Ph}_4\text{C}_4)\text{PdCl}_2$  in 20 ml of dried deoxygenated methylene chloride, and allowed to stand  
15 at room temperature for 24 hrs. This acetylene polymer film was thereafter transferred to another vessel, washed with fresh methylene chloride, and then dried under vacuum. The doped acetylene polymer film thus obtained had an electrical conductivity of  $3 \times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$ .

20 Example 14

An acetylene polymer film was immersed in a solution of 0.2 g of  $p\text{-ClC}_6\text{H}_4\text{N}_2\text{PF}_6$  in 20 ml of dried deoxygenated ethanol, and allowed to stand at room temperature for 24 hrs. This acetylene polymer film was  
25 thereafter transferred to another vessel, washed with fresh

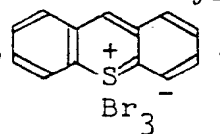
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1 ethanol, and then dried under vacuum. The doped  
acetylene polymer film thus obtained had an electrical  
conductivity of  $1 \times 10^{-4} \Omega^{-1} \cdot \text{cm}^{-1}$ .

## Example 15

5 An acetylene polymer film was immersed in a  
solution of 0.1 g of  $\text{C}_{13}\text{H}_9\text{SBr}_3$  in 20 ml of dried  
deoxygenated methanol, and allowed to stand at room  
temperature for 24 hrs. This acetylene polymer film was  
thereafter transferred to another vessel, washed with  
10 fresh methanol, and then dried under vacuum. The doped  
acetylene polymer film thus obtained had an electrical  
conductivity of  $7 \times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$ .

Said  $\text{C}_{13}\text{H}_9\text{SBr}_3$  means thioxanthylum perbromide  
having the structural formula,



## 15 Example 16

An acetylene polymer film was immersed in a  
solution of 0.1 g of  $\text{Ph}_3\text{C}^+\text{ClO}_4^-$  in 20 ml of dried  
deoxygenated methylene chloride, and allowed to stand at  
room temperature for 24 hrs. This acetylene polymer  
20 film was thereafter transferred to another vessel, washed  
with fresh methylene chloride and then dried under  
vacuum. The doped acetylene polymer thus obtained had  
an electrical conductivity of  $3 \times 10^1 \Omega^{-1} \cdot \text{cm}^{-1}$ .

## Example 17

25 Triphenylmethyl trifluoroacetate was



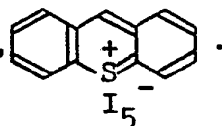
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- 1 synthesized by adding 0.5 g of  $\text{Ph}_3\text{COH}$  to 3 ml of dried deoxygenated trifluoroacetic acid, and in the resulting reaction mixture was immersed an acetylene polymer film, and allowed to stand at room temperature for 24 hrs.
- 5 This acetylene polymer film was thereafter transferred to another vessel, washed with fresh trifluoroacetic acid and then dried under vacuum. The doped acetylene polymer film thus obtained had an electrical conductivity of  $3 \times 10^{-4} \Omega^{-1} \cdot \text{cm}^{-1}$ .
- 10 For comparison, an acetylene polymer film was immersed in 3 ml of deoxygenated trifluoroacetic acid and allowed to stand at room temperature for 24 hrs. The acetylene polymer film was thereafter taken out of the trifluoroacetic acid, and then dried under vacuum.
- 15 The acetylene polymer film thus treated had an electrical conductivity of less than  $10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$ .

## Example 18

- An acetylene polymer film was immersed in a solution of 0.1 g of  $\text{C}_{13}\text{H}_9\text{SI}_5$  in 20 ml of dried deoxygenated methanol and allowed to stand at room temperature for 24 hrs. This acetylene polymer film was thereafter transferred to another vessel, washed with fresh methanol and then dried under vacuum. The doped acetylene polymer film had an electrical conductivity
- 25 of  $8 \times 10^{-4} \Omega^{-1} \cdot \text{cm}^{-1}$ .

Said  $\text{C}_{13}\text{H}_9\text{SI}_5$  means thioxanthylum periodide having the structural formula,



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## WHAT IS CLAIMED IS:

1. An acetylene polymer doped with a dopant selected from the group consisting of a platinum group metal complex, a carbonium salt, an oxonium salt and a parabenzoquinone derivative.
2. A doped acetylene polymer according to claim 1, wherein the dopant is a platinum group metal complex selected from the group consisting of  $(\text{PhCN})_2\text{PdCl}_4$ ,  $(\text{COD})\text{PdCl}_2$ ,  $[(\text{C}_2\text{H}_4)\text{PdCl}_2]_2$ ,  $(\text{Ph}_4\text{C}_4)\text{PdCl}_2$ ,  $(\text{COD})\text{PtCl}_2$ ,  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]\text{H}_2\text{O}$ ,  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$ ,  $(\text{PhCN})_2\text{PtCl}_2$ ,  $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$  and  $\text{Ru}(\text{COD})\text{Cl}_2$  wherein COD stands for 1,5-cyclooctadiene and  $\text{Ph}_4\text{C}_4$  for tetraphenylcyclobutadiene.
3. A doped acetylene polymer according to claim 1, wherein the dopant is a palladium complex.
4. A doped acetylene polymer according to claim 3, wherein the dopant is  $(\text{PhCN})_2\text{PdCl}_2$  or  $[(\text{C}_2\text{H}_4)\text{PdCl}_2]_2$ .
5. A doped acetylene polymer according to claim 1, wherein the dopant is a combination of an anion selected from the group consisting of  $\text{BF}_4^-$ ,  $\text{AlCl}_4^-$ ,  $\text{FeCl}_4^-$ ,  $\text{SnCl}_5^-$ ,  $\text{PF}_6^-$ ,  $\text{PCl}_6^-$ ,  $\text{SbCl}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$  and  $\text{CF}_3\text{CO}_2^-$  with a cation selected from the group consisting of triphenylmethyl ion  $[(\text{C}_6\text{H}_5)_3\text{C}^+]$ , tropylium ion  $(\text{C}_7\text{H}_7^+)$ , acyl ion  $(\text{RCO}^+)$ , triethyloxonium ion  $[(\text{C}_2\text{H}_5)_3\text{O}^+]$ , and dialkoxycarbonium ion  $[\text{RC}(\text{OR}')(\text{OR}'')^+]$  in which R, R' and R'' stand for organic groups.
6. A doped acetylene polymer according to claim 1, wherein the dopant is a combination of an anion selected from the group consisting of  $\text{BF}_4^-$  and  $\text{ClO}_4^-$  with a cation

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selected from the group consisting of triphenylmethyl ion  $[(C_6H_5)_3C^+]$  and triethyloxonium ion  $[(C_2H_5)_3O^+]$ .

7. A doped acetylene polymer according to claim 1, wherein the dopant is a parabenzoquinone derivative
- 5 selected from the group consisting of 2,3-dicyano-5-chloroparabenzoquinone, 2,3-dichlorodicyanoparabenzoquinone, 2,3-dicyano-5-phenylsulfonylparabenzoquinone, 2,3-dicyano-5-chloro-6-phenylparabenzoquinone and 2,3,5,6-tetracyanoparabenzoquinone.
- 10 8. A doped acetylene polymer according to claim 7, wherein the parabenzoquinone derivative has a first half wave reduction potential ( $-E_{1/2}$ ) of less than -0.2 V as measured at 25°C by means of a saturated calomel electrode using  $LiClO_4$  in acetonitrile as the supporting
- 15 electrolyte.
9. A doped acetylene polymer according to any one of claims 1 to 8, wherein the starting acetylene polymer is in the form of film.
10. A process for producing a doped acetylene
- 20 polymer which comprises immersing an acetylene polymer under an inert gas atmosphere in an organic solvent solution of a dopant selected from the group consisting of a platinum group metal complex, a carbonium salt, an oxonium salt and a parabenzo-
- 25 quinone derivative.
11. A process according to claim 10, wherein the immersion is carried out at 10° to 70°C.
12. A process according to claim 10, wherein the

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dopant is a platinum group metal complex selected from the group consisting of  $(\text{PhCN})_2\text{PdCl}_2$ ,  $(\text{COD})\text{PdCl}_2$ ,  $[(\text{C}_2\text{H}_4)\text{PdCl}_2]_2$ ,  $(\text{Ph}_4\text{C}_4)\text{PdCl}_2$ ,  $(\text{COD})\text{PtCl}_2$ ,  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$ ,  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$ ,  $(\text{PhCN})_2\text{PtCl}_2$ ,  $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ , and  $\text{Ru}(\text{COD})\text{Cl}_2$ , wherein COD stands for 1,5-cyclooctadiene and  $\text{Ph}_4\text{C}_4$  for tetraphenylcyclobutadiene.

13. A process according to claim 10, wherein the dopant is a palladium complex.

14. A process according to claim 13, wherein the palladium complex is  $(\text{PhCN})_2\text{PdCl}_2$  or  $[(\text{C}_2\text{H}_4)\text{PdCl}_2]_2$ .

15. A process according to claim 10, wherein the dopant is a combination of a cation selected from the group consisting of triphenylmethyl ion  $[(\text{C}_6\text{H}_5)_3\text{C}^+]$ , tropylium ion  $(\text{C}_7\text{H}_7^+)$ , acyl ion  $(\text{RCO}^+)$ , dialkoxycarbonium ion  $[\text{RC}(\text{OR}')_2^+]$ , and triethyloxonium ion  $[(\text{C}_2\text{H}_5)_3\text{O}^+]$  with an anion selected from the group consisting of  $\text{BF}_4^-$ ,  $\text{AlCl}_4^-$ ,  $\text{FeCl}_4^-$ ,  $\text{SnCl}_5^-$ ,  $\text{PF}_6^-$ ,  $\text{PCl}_6^-$ ,  $\text{SbCl}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$  and  $\text{CF}_3\text{CO}_2^-$ .

16. A process according to claim 10, wherein the dopant is a parabenzoquinone derivative selected from the group consisting of 2,3-dicyano-5-chloroparabenzoquinone, 2,3-dichloro-5,6-dicyanoparabenzoquinone, 2,3-dicyano-5-phenylsulfonylparabenzoquinone, 2,3-dicyano-5-chloro-6-phenylsulfonylparabenzoquinone and 2,3,5,6-tetracyanoparabenzoquinone.

17. A process according to claim 16, wherein the parabenzoquinone derivative has a first half wave reduction potential  $(-E_{1/2})$  of less than  $-0.2$  V as measured

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at 25°C by means of a saturated calomel electrode using  $\text{LiClO}_4$  as a supporting electrolyte in acetonitrile.

18. A process according to claim 10, wherein the organic solvent is selected from the group consisting  
5 of aromatic hydrocarbons, nitrile compounds, nitro compounds, ether compounds, lower alcohols, halogeno compounds, ester compounds, ketone compounds, sulfoxide compounds and lower organic acids and their anhydrides.

19. A process according to claim 10, wherein  
10 the organic solvent is a compound selected from the group consisting of benzene, toluene, xylene, nitromethane, nitroethane, nitrobenzene, acetonitrile, benzonitrile, diethyl ether, tetrahydrofuran, dioxane, anisole, methanol, ethanol, propanol, dichloromethane,  
15 chloroform, chlorobenzene, methylene chloride, trifluoroacetic acid, methyl acetate, ethyl acetate, acetone, acetophenone, dimethylsulfoxide, N,N-dimethylformamide, acetic acid and acetic anhydride.



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# EUROPEAN SEARCH REPORT

0022271

Application number

EP 80103857.1

| DOCUMENTS CONSIDERED TO BE RELEVANT |   |  | CLASSIFICATION OF THE APPLICATION (Int. Cl. 1)   |
|-------------------------------------|---|--|--|
| Category                            | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim                              |  |
| A                                   | <u>US - A - 3 926 907</u> (ENGLE)<br>+ Columns 8,9 +<br>--                    |  | C 08 L 49/00<br>C 08 J 3/20//<br>C 08 K 3/10<br>C 08 K 5/08  |
| A                                   | <u>US - A - 2 351 108</u> (COLLINS)<br>-----                                  |  | C 08 K 5/09<br>H 01 B 1/00   |
|                                     |   |  | TECHNICAL FIELDS SEARCHED (Int. Cl. 2)   |
|                                     |   |  | C 08 L<br>C 08 J<br>C 08 K<br>H 01 B   |
|                                     |   |  | CATEGORY OF CITED DOCUMENTS  |
|                                     |   |  | X: particularly relevant<br>A: technological background<br>O: non-written disclosure<br>P: intermediate document<br>T: theory or principle underlying the invention<br>E: conflicting application<br>D: document cited in the application<br>L: citation for other reasons |
| X                                   | The present search report has been drawn up for all claims                    |  | 6: member of the same patent family, corresponding document  |
| Place of search<br>VIENNA           |   | Date of completion of the search<br>10-10-1980 | Examiner<br>DICHER   |